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published in
Applied Spectroscopy
2006

DOI (link to publisher)
10.1366/000370206778062101

document version
Publisher's PDF, also known as Version of record

Cavity Ring-Down Spectroscopy for Detection in Liquid Chromatography: Extension to Tunable Sources and Ultraviolet Wavelengths

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In earlier studies, it was demonstrated that the sensitivity of absorbance detection in liquid chromatography (LC) can be improved significantly by using cavity ring-down spectroscopy (CRDS). Thus far, CRDS experiments have been performed using visible laser light at fixed standard wavelengths, such as 532 nm. However, since by far most compounds of analytical interest absorb in the ultraviolet (UV), it is of utmost importance to develop UV-CRDS. In this study, as a first step towards the deep-UV region, LC separations with CRDS detection (using a previously described liquid-only cavity flow cell) at 457 and 355 nm are reported for standard mixtures of dyes and nitro-polyaromatic hydrocarbons (nitro-PAHs), respectively. For the measurements in the blue range a home-built optical parametric oscillator (OPO) system, tunable between 425 and 478 nm, was used, achieving a baseline noise of 2.7×10^{-6} A.U. at 457 nm, improving upon the sensitivity of conventional absorbance detection (typically around 10^{-4} A.U.). An enhancement of the sensitivity can be seen at 355 nm as well, but the improvement of the baseline noise (1.3×10^{-5} A.U.) is much less pronounced. The sensitivity at 355 nm is limited by the quality of the UV-CRDS mirrors that are currently available: whereas the ring-down times as obtained at 457 nm are around 70–80 ns for the eluent, they are only 20–25 ns at 355 nm. Critical laser characteristics for LC-CRDS measurements, such as pulse length and mode structure, are given and prospects for going to shorter wavelengths are discussed.

Index Headings: **Cavity ring-down spectroscopy; CRDS; Liquid-only cavity; Absorption detection; Azo dyes; Nitro-polyaromatic hydrocarbons; Nitro-PAHs; Optical parametric oscillator.**

INTRODUCTION

Liquid chromatography (LC) is used in many research areas including chemistry, biochemistry, and environmental sciences. Quite often, the scope of these LC studies is to find traces of compounds or contaminants in complex mixtures. Hence, the development of sensitive detection methods is imperative.

Direct absorbance detection is often the detection method of choice due to its versatility and simplicity. Moreover, since absorbance detection is nondestructive, it can be used in tandem with other detection methods, e.g., mass spectrometry. However, the sensitivity of the method is ultimately determined by the precision at which the relative intensity change $\delta I/I$ can be measured. Since cavity ring-down spectroscopy (CRDS) is based on the measurement of the rate of decay of light exiting a high-finesse cavity rather than $\delta I/I$, it is no longer limited by fluctuations in I. Furthermore, since the light is detected after hundreds or thousands of round-trips through the cavity, the effective sample path length is dramatically increased.

In previous studies, the feasibility of using CRDS as a detector for LC separations was tested and different experimental schemes were explored.[1–4] In the Stanford group a setup based on a double Brewster's angle flow cell was implemented inside a cavity spanning 1 m. Using a pulsed dye laser at 470 nm and a pulsed CRDS detection scheme, a base-line noise of 1.3×10^{-5} A.U. peak-to-peak was obtained for on-line LC separations.[1] In a continuous wave CRDS detection scheme, employing a frequency-doubled diode laser at 488 nm and the same extended-cell layout, the base-line noise for LC could be decreased to 2.7×10^{-7} A.U.[2] In our laboratory we adopted a different approach to the design of the cell. Since any change in ring-down time is induced only within the optical path through the liquid LC detection volume, the optical path length of the absorbance cell was made to coincide with the length of the optical resonator.[3,4] This design involves direct contact of the solvent fluids with the mirror coatings, but this was shown to cause no problems for typical LC separation eluents, such as 50% potassium phosphate buffers in HPLC-grade methanol. CRDS detection in pulsed CRDS schemes at 532 nm and averaging over 1 second led to an LC baseline noise level of 2.7×10^{-6} A.U.[4]

A major drawback of the hitherto proven CRDS detection schemes is in the wavelength limitations. While the method has been demonstrated in the visible wavelength domain, most relevant molecules do not absorb in this range. Since absorbance detection in the ultraviolet (UV) is almost universal in LC, it is relevant to extend CRDS detection to shorter wavelengths. Both in the case of a small liquid-only cavity and in the design with the Brewster cell inside a larger resonator, high-reflectance coatings are required to obtain detection sensitivities by CRDS that are competitive with conventional absorption detection. The present technology of manufacturing highly reflective coatings is a limiting factor at UV wavelengths, although significant progress is currently being made.

For the CRDS measurements at 457 nm, azo dyes were selected as model analytes. We then proceeded to CRDS detection at 355 nm, in order to develop a sensitive method for nitro-substituted polycyclic aromatic hydrocarbons (PAHs). Nitro-PAHs comprise a group of (non-fluorescing) environmental pollutants that are highly carcinogenic compounds.[5–7] Whereas the mutagenic activity of their parent PAHs is indirect, nitro-substituted and oxygenated PAHs are direct acting mutagens. For example, the mutagenic activity of tobacco smoke can be correlated to the amount of subtituted PAHs. Nitro-PAHs originate from primary emission sources like exhaust gases (2-nitrofluorene or 1-nitropyrene) or unsubstituted polyaromatic hydrocarbons can be nitrated in the atmosphere (2-nitrofluoranthene or 2-nitropyrene).[8] In the environment, these nitro-PAHs can be found in air particles and aerosols. Many studies concerning the amount of nitro-PAHs in air, particularly in urban air samples, have been conducted.[8–10]

Received 7 April 2006; accepted 25 May 2006.

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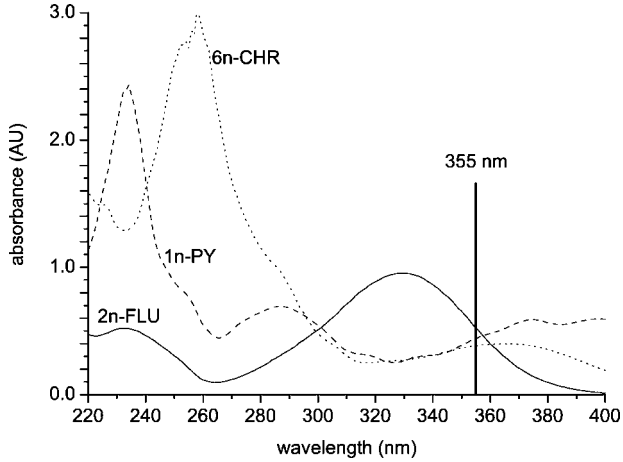

FIG. 1. Absorbance spectra of the nitro-PAHs used in this study. Concentrations were 50 μM in eluent (80% methanol, 20% water).

To determine nitro-PAHs in environmental samples, absorption detection is generally not sufficiently sensitive. Therefore, a post-column derivatization to amino-PAHs is commonly used in order to use the more sensitive fluorescence detection technique.[11–13] Of course, such an approach, although quite successful, complicates the detection system. That is why absorption detection modes such as CRDS might become of interest.

Here we report on extending CRDS methods for on-line LC detection progressively toward shorter wavelengths. Specifically for the blue region (420–480 nm), a tunable source of pulsed radiation, based on a compact optical parametric oscillator (OPO), was built and applied, demonstrating sensitive LC detection of azo dyes. In a second experiment it is demonstrated that UV-CRDS (at 355 nm) is feasible for sensitive detection of nitro-PAHs. The focus of the present work is on CRDS method development as such, where only isocratic separations are considered. Requirements as to the laser characteristics will be discussed.

EXPERIMENTAL

Chemicals and Liquid Chromatography Separations. The LC separation of the azo dyes was carried out isocratically, and the eluent was 50% (v/v) 10 mM potassium phosphate buffer (pH = 7.4) in MilliQ water, 50% HPLC-grade methanol. For the separation of the nitro-PAHs, the eluent was 80% methanol, 20% MilliQ water. The azo dyes ($\varepsilon_{457} = 1.4 \times 10^4$ $M^{-1}cm^{-1}$ for Direct Violet 17 (891.8 g/mol), $\varepsilon_{457} = 1.5 \times 10^4$ $M^{-1}cm^{-1}$ for Direct Red 10 (697.7 g/mol), and $\varepsilon_{457} = 3.6 \times 10^4$ $M^{-1}cm^{-1}$ for benzopurpurine (724.7 g/mol)) and the nitro-PAHs ($\varepsilon_{355} = 10.2 \times 10^3$ $M^{-1}cm^{-1}$ for 2-nitrofluorene, (211.22 g/mol), $\varepsilon_{355} = 8.7 \times 10^3$ $M^{-1}cm^{-1}$ for 1-nitropyrene (247.26 g/mol), and $\varepsilon_{355} = 7.3 \times 10^3$ $M^{-1}cm^{-1}$ for 6-nitrochrysene (273.29 g/mol)) were all obtained from Sigma-Aldrich (Germany). Absorbance spectra of the nitro-PAHs are shown in Fig. 1.

For both experiments, the flow rate was set to 0.8 mL/min with an Applied Biosystems 400 solvent delivery system; 50 μL of sample (dissolved in eluent) was injected using a six-port injection valve. The column was a Chromsep Microspher (Varian) C_{18} 100 × 4.6 mm (length × internal diameter) reversed-phase column equipped with a guard column. For comparison, a similar separation was performed using a conventional UV-visible absorbance detector (Separations, Applied Biosystems 759a, 8 μL U-shaped flow cell with 8 mm optical path length) that was set at the laser wavelength of the CRDS measurements.

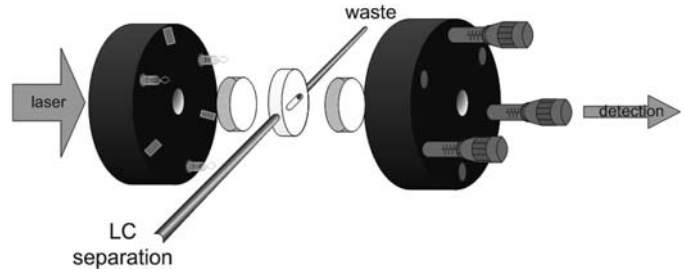

FIG. 2. Schematic diagram of the liquid-only cavity flow cell (not to scale). The boundaries of the flow cell are formed by the high-reflectivity mirrors, clamped leak-tight to the sides of a silicon rubber spacer. Capillary tubing is inserted in the spacer for introducing the liquid flow. During operation the mirror separation is 2 mm, and the detection volume is 12 μL.

Requirements for Cavity Ring-Down Spectroscopy. As discussed previously,[4] the bandwidth of the laser source is an important parameter for successful operation of CRDS in a miniature cavity of length $L = 2$ mm as in the present liquid-only cell design as depicted in Fig. 2. For such a cavity the longitudinal mode spacing is on the order of 2 cm^{-1}, while the mode width $\delta\nu$ is less than 10^{-4} cm^{-1} for high-finesse resonators built from mirrors with reflectivities $R \geq 99.9\%$. It is essential for a steady optical coupling of subsequent laser pulses into a passive resonator (that may be subject to temperature drift) that the bandwidth of the laser is sufficiently large: the choice of mirrors with radii-of-curvature (r.o.c.) strongly deviating from the chosen cavity length, such that the cavity is non-confocal and supports large numbers of transversal modes, improves the operation. Previously it was shown under conditions of $\lambda = 532$ nm and mirrors with r.o.c. = 50 mm that stable operation without mode-beating in the transmission of the miniature cavity could be established for laser bandwidths $\Delta\nu$ of 1 cm^{-1}, but for $\Delta\nu = 0.01$ cm^{-1} severe mode beatings prevented stable operation. It should be noted that such a bandwidth does not put any restrictions to CRDS in the liquid phase where molecular absorption spectra show spectral bandwidths of more than 100 cm^{-1}. For this work, our choices for laser systems to be operated at the desired wavelengths of 355 nm and in the blue range were based on these considerations. In addition, the laser pulses should be of sufficiently short duration, i.e., much shorter than the obtainable ring-down transients, to not affect the detection sensitivity.

Cavity Ring-Down Spectroscopy Measurements at 457 nm. For the measurements in the blue region a pulsed laser source was developed that matches the bandwidth and temporal characteristics required for CRDS measurements in the liquid-only cell design. A further practical requirement is to match the tunability of the source to the range of high reflectivity of the CRDS mirrors.

Such characteristics can be met by an optical parametric oscillator (OPO), based on a β-BaB_2O_4 (BBO) nonlinear crystal that is pumped at 355 nm. For most spectroscopic applications of OPOs complex pump geometries, with injection-seeding[14] and oscillator-amplifier combinations,[15] are developed to attain single-longitudinal mode operation. However, in a simplified scheme of an OPO, without any optical element besides the BBO crystal and the two mirrors

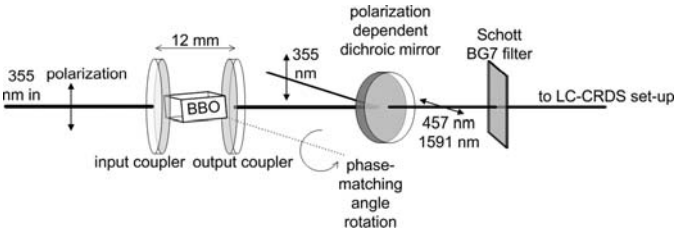

FIG. 3. Schematic diagram of the wavelength-tunable OPO laser light source delivering laser pulses in the range 425–475 nm at a bandwidth of around 0.2 nm.

forming the resonator, pulses of typical bandwidths $\Delta\nu$ in the range of 0.25 nm (or 10 cm^{-1}), the desired characteristics for the liquid-only cell CRDS experiments, can be produced. The optical layout of such a home-built OPO system is shown in Fig. 3. In fact, the system is identical to the power-amplifying OPO that was used in combination with a grazing-incidence optical parametric oscillator in Ref. 14; here it is used as a stand-alone oscillator and, in the absence of injection-seeding, delivers optical bandwidth within the full phase-matching opening angle of the BBO-OPO. The cavity length only slightly exceeds the length of the crystal (10 mm) and is built from an in-coupling plane mirror transmitting the UV of the pump source at 355 nm with a reflectivity of 90% in the blue range, and a plane output coupler with $R = 70\%$. The BBO crystal is cut for type-I phase matching at an angle of 30° and is manually rotated. The limited wavelength coverage of the OPO is due to the reflectivity properties of the mirrors spanning the cavity. The 355 nm pump light is dumped behind the OPO using a polarization-dependent dichroic mirror, while the remaining light at 355 nm and at the OPO idler wavelength are filtered behind the OPO with a Schott BG7 filter.

This OPO is pumped by the third-harmonic output of a narrow-bandwidth Coherent Infinity 40–100 Nd:YAG laser with a pulse duration of 2.4 ns and a repetition rate that can be set between 10 and 100 Hz. The operation of the simple OPO design, displayed in Fig. 3, was determined in a set of characterization measurements. With pump powers in the range 25–50 mJ/pulse a conversion efficiency of typically 20% is obtained across the range, where the finesse of the OPO is on the order of 20. The Coherent pump laser has the special property, due to a phase-conjugate mirror inside the amplifier system, that the beam profile is unaffected by thermal effects, when the repetition rate is varied in the range 10–100 Hz. The bandwidth of the OPO output steadily increases from 0.15 to 0.25 nm (or 8.5 to 11 cm^{-1}) over the interval 420–480 nm, while the pulse duration of the output pulses smoothly increases from 4.2 to 4.6 ns.

The CRDS setup was similar to the one described in our previous studies.[3,4] Mirrors with $R \geq 99.993\%$ over a broad range from 450 to 480 nm, 200 mm (entrance mirror)/10 mm (exit mirror) radius of curvature were obtained from REO Inc. (Boulder, CO). In order to create the 12 μL flow cell, a 2 mm thick silicon rubber spacer with a near-elliptical hole was pressed leak-tight between the two mirrors. Flow was introduced via capillary tubing inserted in the spacer. The mirrors were in direct contact with the liquid flow. Although no noticeable degradation of the mirror quality was observed during a day's work, the mirrors needed cleaning with methanol at the end of each day and were stored in a desiccator overnight.

Detection of the optical transient behind the cavity was done

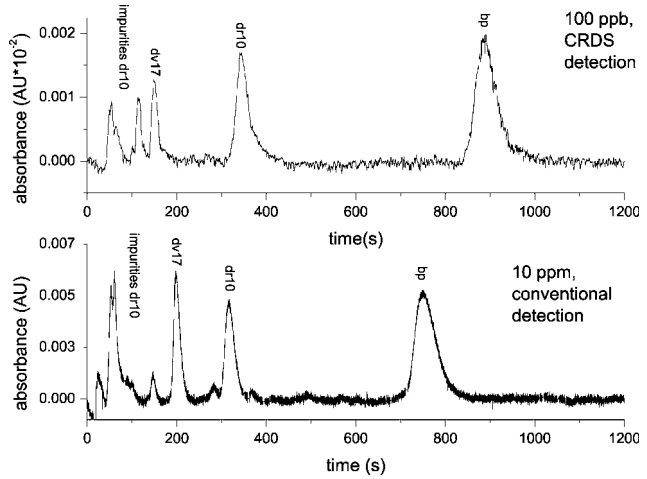

FIG. 4. Chromatograms of a standard mixture of Direct Violet 17, Direct Red 10, and benzopurpurine as obtained for (**top**) CRDS detection and (**bottom**) conventional absorbance detection at 457 nm. Injected concentrations: (**top**) 100 ppb, and (**bottom**) 10 ppm. Retention time differences are due to differences between eluents used in the different runs.

with a 4 GHz bandwidth photodiode (PHD400, Becker & Hickl) together with a 35 dB 1.8 GHz amplifier (Becker & Hickl). An auxiliary photodiode was employed to trigger the detection system. The transients were registered by a fast oscilloscope (Tektronix 5104 1 GHz) at a maximum sampling rate of 5 Gs/s, storing 2000 data points, covering a 400 ns time trace that typically corresponds to 5τ.

In measurements characterizing the mirrors, ring-down transients were probed to verify the mirror reflectivities in the empty-cell configuration. At wavelengths $\lambda < 450$ nm decay times of 25 ns were obtained, which gradually increased to 120 ns between 470 and 480 nm, at the optimum reflectivity of the mirror set. Despite the fact that 457 nm (chosen in order to obtain sufficient intensities on the photodiode) is somewhat displaced from the optimum, satisfactory results have been obtained at this wavelength. Typical decay transients during LC-CRDS operation at a preset wavelength of 457 nm were on the order of 75–80 ns; the pulse duration of the OPO pulses (4.5 ns) does not restrict the accurate determination of τ and therewith the sensitivity.

Cavity Ring-Down Spectroscopy Measurements at 355 nm. The measurements at 355 nm were performed with the output of a Q-switched, mode-locked and frequency-tripled Nd:YAG laser (Quantel); the pulses have a duration of 100 ps, the wavelength of the system is fixed, and the bandwidth at 355 nm is several cm^{-1}. Since relatively short ring-down times were expected, this laser was preferred over the above-mentioned pump laser because of its shorter pulse length. In combination with a sampling scope of 1 GHz analog bandwidth (Tektronix 5104; 5 GS/s) and a photomultiplier tube (Hamamatsu) a response time of 2 ns full-width at half-maximum (FWHM) is achieved, sufficient for the analysis of typical decay transients in the 15–20 ns range. Again, the same liquid-only flow cell was used, now assembled from two highly reflective (at 355 nm) concave mirrors (Layertec, $R \geq 99.95\%$, radius of curvature = 50 mm).

RESULTS AND DISCUSSION

Typical chromatograms for the dye mixture detected at 457 nm—where the dyes show extinction coefficients in the 10^4

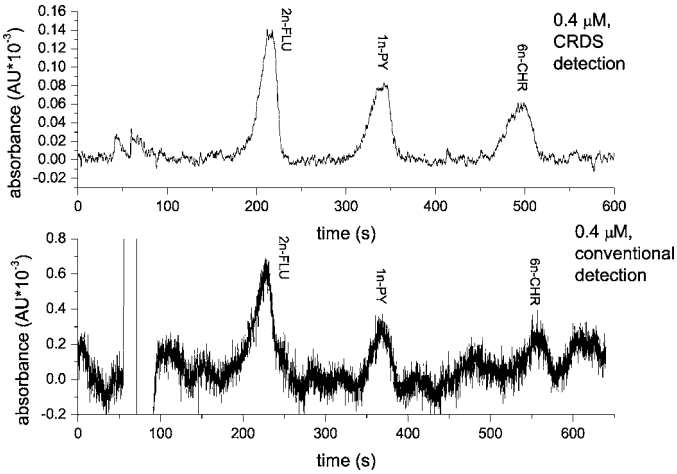

FIG. 5. Chromatograms of a standard mixture of 2-nitrofluorene, 1-nitropyrene, and 6-nitrochrysene as obtained for (**top**) CRDS detection and (**bottom**) conventional absorbance detection at 355 nm. Injected concentrations: 0.4 μM for both chromatograms.

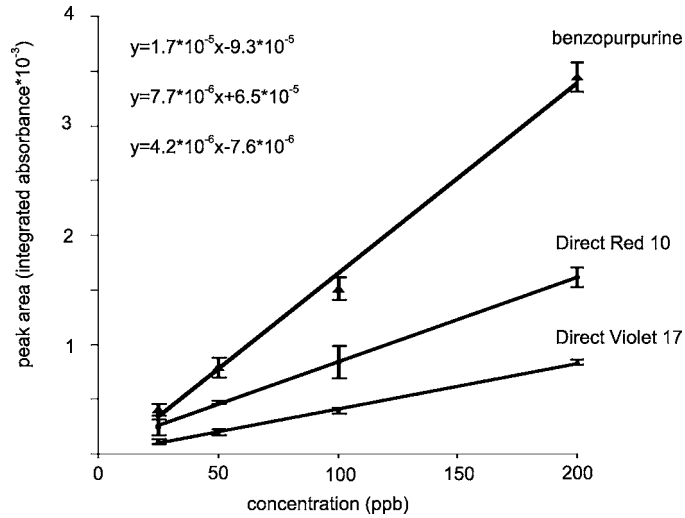

FIG. 6. Calibration curves of Direct Violet 17, Direct Red 10, and benzopurpurine show that CRDS detection is linear up to at least 200 ppb. Each concentration was measured three times; the error bars show the standard deviation. R^2 values of the regression lines are 99.5% or better.

$M^{-1}cm^{-1}$ range—are shown in Fig. 4; the nitro-PAH mixture detected at 355 nm—a suitable wavelength, see Fig. 1—are shown in Fig. 5. In order to obtain these chromatograms in CRDS, the measured ring-down times are scaled to absorbance units as used in the Lambert–Beer law (εCL) where ε is the molar extinction coefficient in $M^{-1}cm^{-1}$, C is the concentration in M, and L is the absorbance path length (2 mm in our case). The absorbance due to the analyte follows directly from the fitted 1/*e* decay times:

$$\alpha_{\text{anal}} = 2.303\varepsilon C = \left(\frac{n}{c}\right)\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

where τ_0 is the fitted 1/*e* decay time when only eluent is present in the cavity; this reduces to τ if an analyte passes the cavity, n is the refractive index of the eluent, and c is the speed of light. Data were averaged over one second and a baseline ($1/\tau_0$) was subtracted.

Chromatographic band broadening due to imperfect flow profiles inside the liquid-only CRDS flow cell is estimated at 15%, which is generally acceptable from a practical point of view. Nonetheless, presumably the difference in chromatographic resolution explains why the impurities coming from Direct Red 10 are fully resolved in the lower panel of Fig. 4, but not completely in the upper panel of Fig. 4. Furthermore, note the different vertical scale in the two chromatograms: it accounts for the 100-fold concentration difference and the 4-fold difference in path lengths, i.e., 2 mm and 8 mm, respectively. The concentration detection limit of our LC-CRDS setup at 457 nm ranges from 12 ppb (17 nM) for Direct Red 10 to 20 ppb (28 nM) for benzopurpurine.

Ring-down times for the baseline at 457 nm were typically between 70 and 80 ns (depending on the alignment and the cleanliness of the mirrors), which means that the light as detected after one ring-down time has traveled 15–18 meters (7500–9000 reflections) inside the cavity. The noise level of our CRDS detection at 457 nm was typically less than 2.7×10^{-6} A.U., much lower than our conventional absorbance detector (1×10^{-4}) and comparable to the best instruments available. The improvement in detectability is clear when one compares the signal-to-noise (S/N) ratio in the upper panel of Fig. 4, which is obtained for a hundred-fold lower concentration (100 ppb) with that in the lower panel with conventional detection (10 ppm). The used OPO system has the advantage of increasing the repetition rate to 100 Hz, allowing for more data averaging in comparison with the 10 Hz laser used at 355 nm.

The UV-CRDS system at 355 nm was tested using a mixture of three nitro-PAHs. The extinction coefficients are around 10^4 $M^{-1}cm^{-1}$ (see Fig. 1). The resulting chromatograms are shown in Fig. 5 for CRDS detection (top) and conventional detection (bottom). With the available mirrors at 355 nm, the ring-down times for the baseline are 3- to 4-fold less favorable (i.e., 20 to 25 ns), so that only 100 to 125 data points can be sampled at 5 Gs/s to cover the relevant range of five decay transients. As a consequence the on-line fitting routine yields a less accurate value of τ, and hence a restricted detection limit compared to 457 nm CRDS.

The peaks in the chromatograms can be fitted by a Gaussian function, and as expected, the peak areas in the chromatograms show a linear dependence on the injected concentrations (see Fig. 6). The slopes of the regression lines are in accordance with the extinction coefficients of the azo dyes at 457 nm. The linear dynamic range of the LC-CRDS setup extends from the detection limit (around 12 ppb) up to 200 ppb; at higher concentrations the ring-down transient becomes relatively short and the decay can no longer be fitted properly.

Similar plots were obtained for the nitro-PAHs (see Fig. 7). The different slopes are roughly in line with the extinction coefficients at 355 nm, although they do not exactly match, a feature that we did not investigate any further. The limits of detection are determined to be around 75 nM for 2-nitrofluorene, 100 nM for 1-nitropyrene, and 150 nM for 6-nitrochrysene.

CONCLUSION

Sensitive liquid-phase CRDS detection using a liquid-only cavity flow cell is demonstrated at 457 nm and is competitive with the best instruments available. The baseline noise is only 2.7×10^{-6} A.U., distinctly lower than that obtained for

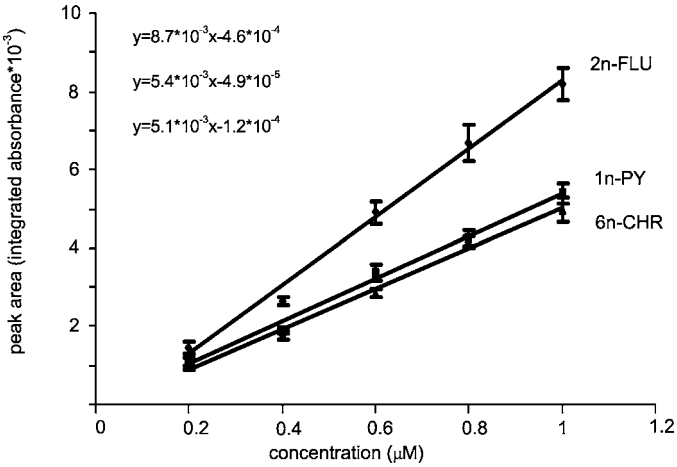

FIG. 7. Calibration curves of 2-nitrofluorene, 1-nitropyrene, and 6-nitrochrysene show that CRDS detection is linear up to at least 200 ppb. Each concentration was measured three times; the error bars show the standard deviation. R^2 values of the regression lines are 99.2%.

conventional absorbance detectors where the baseline noise is typically of the order of 10^{-4} A.U.

The gain in sensitivity at 355 nm (baseline noise is 1.3×10^{-5} A.U.) is less than in the blue range, although the difference in detection performance between CRDS and conventional UV absorbance detection as visualized in Fig. 5 is still quite appealing. As regards further extension of the CRDS detection techniques towards the UV region it should be noted that the difference in sensitivity between 355 nm and 457 nm is mainly due to the limited reflectivity of the 355 nm mirrors at hand. There are no other main hindrances.

In gas-phase applications the CRDS technique was recently extended to deep-UV wavelengths. Sneep et al.[16] performed measurements at wavelengths as short as 197 nm with mirrors of $R = 97\%$, Karaiskou et al.[17] covered the range of 200–205 nm with better quality mirrors of $R = 98.5\%$ and Wang et al.[18] used mirrors of $R = 99.85\%$ at 283.5 nm. For the application in LC-CRDS with the present liquid-only cell geometry a mirror quality of $R \geq 99.95\%$ is demonstrated to yield absorbance detection limits better than for conventional LC absorbance detectors. Suitable wavelengths would be 248 nm and 266 nm, covering the absorption maxima of many relevant molecules, and coincident with the fixed wavelengths of standard lasers (the KrF excimer laser and the fourth harmonic of the Nd:YAG laser), available in many laboratories.

Whereas UV-CRDS measurements in the gas phase start to become successful,[16,18] liquid-phase UV-CRDS is hampered by the rather stringent constraints on required mirror reflectivities, which can currently not yet be met at wavelengths in the deep UV.

ACKNOWLEDGMENT

Financial support from the Netherlands Foundation for Fundamental Research of Matter (FOM) is gratefully acknowledged.

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